Experimental Investigation and High Resolution Simulator of In-Situ Combustion Processes

Quarterly Report

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Abstract

Accurate simulation of in-situ combustion processes is computationally very challenging because the spatial and temporal scales over which the combustion process takes place are very small. In this current and **thirteenth** report, we report on our continuing development of a Virtual Kinetic Cell model and our continuing experimental program.

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1. Introduction

In-situ combustion, or air injection, is the process of injecting oxygen into oil reservoirs to oxidize the heaviest components of the crude oil and enhance oil recovery through the heat and pressure produced. The emphasis of this work is to study and model numerically in situ combustion processes. The ultimate objectives are to provide a working accurate, parallel in situ combustion numerical simulator and to better understand the in-situ combustion process when using metallic additives and/or solvents combined with in situ combustion. For this purpose, experimental, analytical and numerical studies are conducted.

This report presents results of the first quarter of the fourth year of this project.

2. Executive Summary

2.1. Personnel

Current personnel include Prof. Margot Gerritsen (PI), Prof. Tony Kovscek (Co-PI), Dr. Louis Castanier (Technical manager), as well as our graduate student Mr. Rotimi Awoleke (MSc student). We have also continued collaboration with Mr. Morten Kristensen (PhD student) from the Technical University of Denmark, and his advisors Prof. Erling Stenby and Prof. Michael Michelsen.

2.2. Important accomplishments

Numerical work: development of the Virtual Kinetic Cell Model

In previous reports we outlined the design of a Virtual Kinetic Cell model (VKC), which we are using to design suitable numerical integrators for the stiff kinetics in ISC processes, and to investigate the interaction between kinetics and phase behavior.

The Virtual Kinetic Cell (VKC) was developed in [1] and further extended in [2]. The VKC models a porous media system with multiple fluid phases in thermodynamic equilibrium and kinetically driven chemical reactions. In the initial model, the phase behavior description was based on composition independent equilibrium factors. This assumption was later relaxed, and the model now accounts for full phase equilibrium based on an equation-of-state (EoS).

We implemented two types of reaction models: a minimal model, which includes the minimal realistic set of 6 components and corresponding reactions to represent ISC behavior as given below, and a SARA-based model containing 14 components. Both models were discussed in detail in previous quarterly reports. The SARA model is also detailed in [3-5].

In this quarter, we extended the phase detection algorithm to handle full phase equilibrium described by an Equation of State (EoS). We consider the general case with three fluid phases, where the water phase consists of water only and the water component partitions between the water and gas phases. The remaining fluid components partition between the oil and gas phases. There are 7 different phase states with 14 possible switches between states. Each switch has an associated event function, which, when satisfied, triggers the switch to a different state.

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When hydrocarbon components are present in both the oil and gas phases, the equilibrium conditions are solved to determine phase fractions and compositions. When water is present both as liquid and vapour, the equilibrium condition

$$\hat{f}_w^w = \hat{f}_w^g .$$

is solved for water, where the fugacities of water in the water and gas phases are, respectively, $\hat{f}_w^w$ and $\hat{f}_w^g$.

Naturally, some of the phase changes are more likely than others and we will focus mostly on changes involving the oil and gas phases. Since water does not affect kinetics directly, it is expected that changes associated with the water phase will impact integration robustness to a lesser extend than changes associated with the hydrocarbon phases. The condition for liquid water drop-out from a water containing gas phase is that the chemical potential (or

equivalently the fugacity) of water in the water phase is less than the chemical potential of water in the gas phase. In terms of fugacities we have

$$0 < \hat{f}_w^g - \hat{f}_w^w,$$

which is the event function we will monitor. The event function for disappearance of the water phase can be simply written in terms of the amount of liquid water, n_w^w, as

$$0 < n_w^w,$$

where n_w^w is computed as the difference between the total amount of water and the amount of water in the gas phase.

For phase changes involving the oil and gas phases, disappearance of a phase is detected by monitoring phase fractions. In two-phase oil-gas regions we solve directly for the molar gas phase fraction, β. The gas phase fraction defines the event functions for switches to single phase oil or gas. As mentioned in previous reports, the event detection algorithm is based on the discontinuity locking principle requiring the existence of a smooth continuation across the phase boundaries. For changes to single phase oil or gas we exploit the existence of the negative flash [6] in an extended region around the phase envelope.

Detecting a change from single phase gas or oil to a two-phase oil-gas region is more involved for the EoS based approach than for the constant K-value approach. A given mixture is stable as a single phase if, and only if, the total Gibbs energy is at its global minimum. Detecting phase instability requires a stability analysis, which in principle involves a global search in composition space [7]. Therefore, no event function exists that can be evaluated explicitly to determine a change to a two-phase region. Instead, the event function is defined implicitly as the outcome of a stability analysis, which considerably increases the complexity of the problem.

3. Experimental

The experimental program is focused on the proof of concept for (i) water-soluble metallic salts to improve fuel lay down and enhancement of combustion performance as well as (ii) a new recovery concept that combines cyclic solvent injection and in-situ combustion to remove any solid precipitation resulting from the solvent.

Metallic additives may be attractive for heterogeneous and fractured reservoir settings. The catalytic effect engendered by additives may aid combustion in such difficult reservoirs. For this phase of our study we obtained reservoir core with residual oil and an ample supply of crude oil. Scanning electron microscopy (SEM) confirms that the rock grains are consistent with sandstone lithology. The crude oil is a 19.7°API sample. Experiments are planned using crude oil and sand from a quarry, crude oil and reservoir matrix, and reservoir matrix alone. Two categories of experiments are planned: ramped temperature oxidation (i.e., kinetics cell) to obtain the kinetics of combustion combustion-tube runs. The former helps in providing information about the reactions occurring, their rates and their temperature and pressure dependencies. The latter helps in understanding whether a stable combustion front is formed as well as the spatial and temporal propagation of such a fully-developed combustion front. To date studies have focused on ramped temperature oxidation to establish that the oil should/should not combust.

Figure 1 is a graphical summary of the experimental equipment. The combustion tube measures the ability of a combustion front to propagate through a given combination of crude oil, water,

and porous medium. The kinetics cell is used to characterize activation energies of combustion as well as oxygen consumption. The combustion tube, or alternately the kinetics cell, is coupled to a gas analyzer, traveling thermocouple, and data logging system. As the study has so far examined kinetics, our discussion focuses on the apparatus for ramped temperature oxidation.

Briefly, the gas analyzer collects effluent gas composition. This is a compact gas analyzer, measuring oxygen, carbon dioxide, carbon monoxide, and methane concentration. Measurements are recorded once per minute. The outlet streams from the analyzer are vented. Oxygen and nitrogen are provided by gas cylinders and metered using a mass flow controller. Temperatures are recorded in the kinetics cell tests as measured in the center of the cell. The kinetics cell is a thick-walled stainless steel (316) cylinder that is 13.3 cm long and 4.82 cm (O.D) in diameter. The cylinder was sealed by means of knives and annealed copper gaskets. The 0.76 mm (0.030 in) knives were machined into the end face of the cylinder and the endcaps. With pressure at the two ends, the knives on the end of cylinder and the endcaps cut into the gaskets providing a contact seal. Air is injected from the bottom of the cell. Prior to injection, air flows through coiled 3.2 mm (1/8 in.) tubing and is preheated. On the top of the cell air exits and the temperature is measured.

The kinetics cell is packed with a mixture of oil, water, and sand. Two thin-walled stainless steel cups are put inside the kinetics cell. The upper cup is 7.1 cm long with I.D of 2.7 cm. This cup is filled with the oil and sand mixture. The lower cup is filled with dry sand. It serves as a preheater and disperses the inlet air to obtain one-dimensional air flow. Both cups are perforated on the bottom to allow air flow. Sand migration is prevented by 200-mesh stainless steel screens placed across the bottom of each cup. The oil sample was used as received. It is 19.7° API. The reservoir matrix as received still contained hydrocarbon. Reservoir core was crushed to break the rock into sand grains.

4. Results and discussion

4.1. Numerical work: development of the Virtual Kinetic Cell Model

In this section we carry out studies to explore the sensitivity of the kinetics to phase behavior and compare constant K-values vs an EoS approach based on the Peng-Robinson equation. We consider both the minimal reaction model and the SARA based reaction model.

Figure 2 compares the simulation results for a ramped temperature experiment using the minimal reaction model. Clearly, the reaction paths are quite different for the two phase behavior treatments. The K-value approach over-predicts the oil volatility leading to an earlier oil phase disappearance. Since oil components only react in the oil phase, a common assumption in ISC reaction models, the early disappearance of the oil phase results in only a small amount of coke being formed by cracking of the heavy oil, which subsequently affects the oxygen consumption.
Results for a similar experiment using the SARA based reaction model are shown in Figure 3. The concentration trajectories for the base components (saturates, aromatics, resins and asphaltenes), which are present in the initial oil, vary only little with the phase behavior treatment. The trajectories for aromatics and saturates are shown in the figure, but we observe similar behavior for resins and asphaltenes. The main difference between the PR EoS and K-values is in prediction of phase behavior for the oil based LTO products. The K-value data simply

assumes that these components stay in the oil phase, whereas in the PR EoS treatment they are free to partition between the oil and gas phases. This significantly impacts the saturation trajectories in the last part of the simulation. In the K-value approach, the OxdResAr and OxdSat components are consumed in combustion reactions, whereas in the PR EoS approach they vaporize and leak out of the cell before combustion, which explains the observed difference in oxygen consumption rate in the last part of the simulation. Due to the assumption of non-volatile components in the K-value data, a comparison to the PR EoS approach must be interpreted carefully.

The two competing mechanisms for oil component ``consumption'' are the chemical reactions and vaporization. Since the experiments are carried out under controlled temperature, the main indicators for ignition are the oxygen consumption rate and the amount of oil components consumed in reactions relative to the amount which vaporizes. For the PR EoS approach more than 90% of the HO component is consumed in reactions, either in direct oxidation or in cracking. For the K-value approach, on the other hand, only 40% is consumed in reactions and the rest vaporizes. This example clearly illustrates a strong sensitivity to the phase behavior treatment. The sensitivity is partly attributed to the common assumption that components only react in one of the fluid phases, which leads to a strong dependency of the kinetics to the distribution of components between phases as governed by phase behavior. A similar investigation for the SARA based reaction model, measuring the relative amounts of each component consumed in reactions and vaporized, shows less sensitivity to the phase behavior treatment. In this case, both phase behavior models predict only a small amount of vaporization of the components present in the initial oil, thus leading to similar profiles for the oxygen consumption.

4.2. Experimental work

First the crushed reservoir sample was washed with toluene to extract any residual hydrocarbons. The cleaned reservoir matrix was placed in the kinetics cells and subjected to regular test procedures. This test established that the matrix was indeed inert. Next, ramped temperature oxidation experiments were conducted on the as-received crushed reservoir matrix, reservoir matrix saturated with crude oil, and crude oil saturated quarry sand with added clay.

Figure 4 shows the temperature increase versus time. Exothermic reactions are evident around 145 minutes where the temperature elevates to about 450 °C. The temperature increase from about 170 minutes onward is due to the system heater. Figure 5 also illustrates good kinetic performance of this crude. It plots the effluent gas concentration as well as the oxygen consumption from the kinetics cell versus the cell temperature. The experiment is conducted with an excess of oxygen and so the oxygen consumption remains low except at the temperatures corresponding to combustion reactions. Hence, the increase in oxygen consumption around 320 °C and 410 °C in this figure. These temperatures correspond roughly to low temperature oxidation and high temperature oxidation portions. The concentration of carbon monoxide is generally quite low indicating effective combustion of the oil.

The results in Fig. 5 have been processed to obtain the kinetics of combustion. The activation energy (E_A/R) is about 8000 K for the low temperature oxidation reaction and about 13,000 K for the high temperature oxidation reaction. These values are typical of a heavy oil. Table 1 is a partial summary of the kinetics results. Mixture refers to a crude oil mixed with quarry sand and clay, additive refers to aqueous metallic salt mixed added to the crude oil quarry sand mixture.

	Pressure (psig)	Ea/R (K) LTO
Mixture	50	6700
Mixture+Additive	50	7600
Crushed Core	200	8000
Crushed Core+Oil	200	7400
Crushed Core+Oil+Additive	200	6000

Table 1. Activation energies for various mixtures

From the results in Table 1. it is fairly clear that the activation energy of the crushed core, crude oil additive system is the least. Comparison of mixture and additive and crushed core and additive must be done with care as the system pressure is different. Finally, results do not suggest that this oil will self ignite and so some sort of external ignition device is needed.

5. Conclusions

We have made excellent progress with study of the sensitivities of kinetics to phase behavior representations. We have shown clearly that kinetics, and possibly performance prediction of ISC processes, can depend very strongly on phase behavior and extreme care must be taken when implementing a ISC model. We are currently in the process of further analyzing these sensitivities and will report on those in the next quarterly. We emphasize that in the current work we have emphasized robustness of the algorithm, but we plan to address efficiency in the near future.

Regarding the experiments, we must complete the data analysis of the ramped temperature oxidation studies. The tests were conducted at pressures of 50, 200, and 290 psig and so the effect of pressure must be deconvolted. Furthermore, a series of tube runs are planned including:

1. combustion of crushed reservoir matrix alone (homogeneous)
2. combustion of crushed reservoir matrix saturated with crude oil
3. combustion of crude oil in a heterogenous porous medium constructed from uncrushed pieces of reservoir core surrounded by crushed reservoir matrix.

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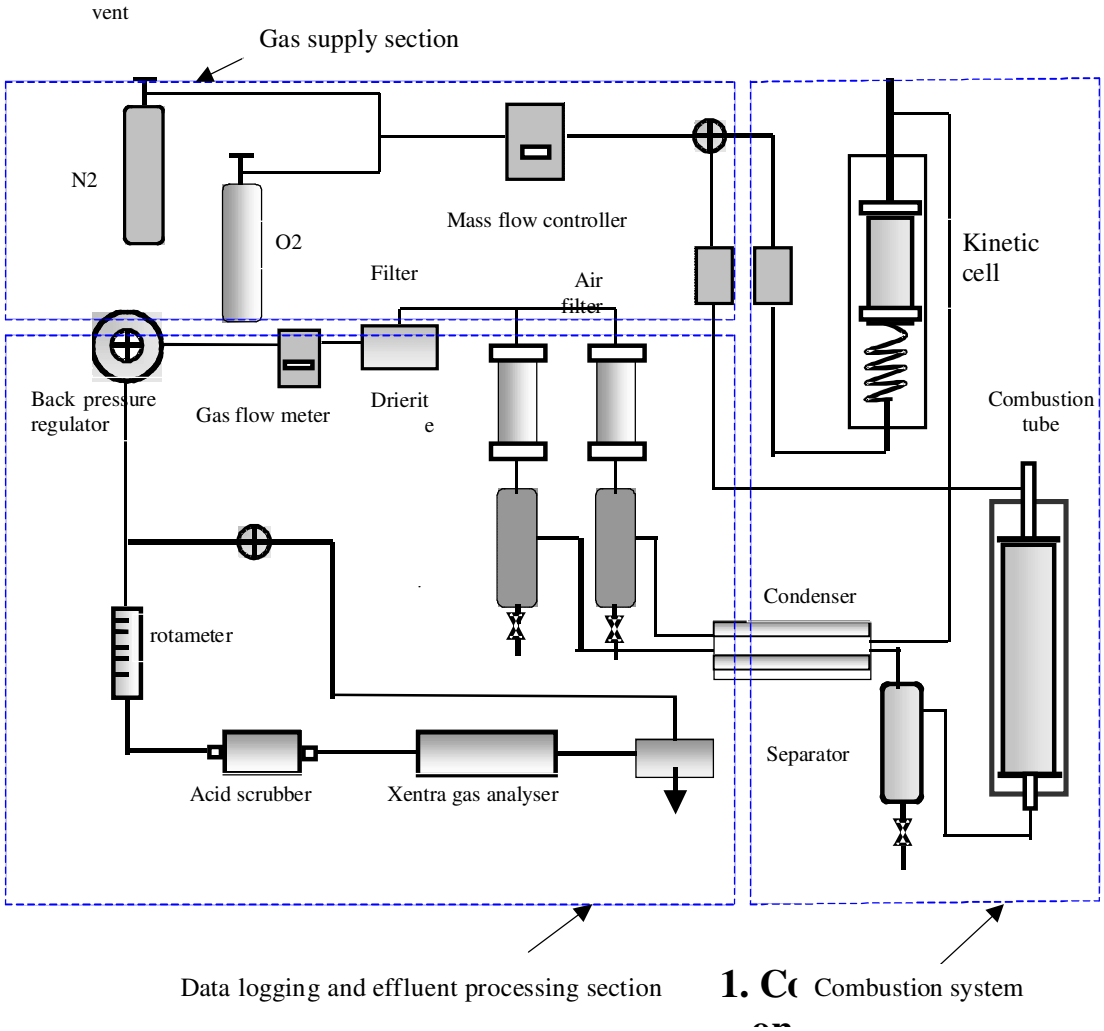

Figure 1. Experimental set-up for kinetic cell and combustion tube experiments.

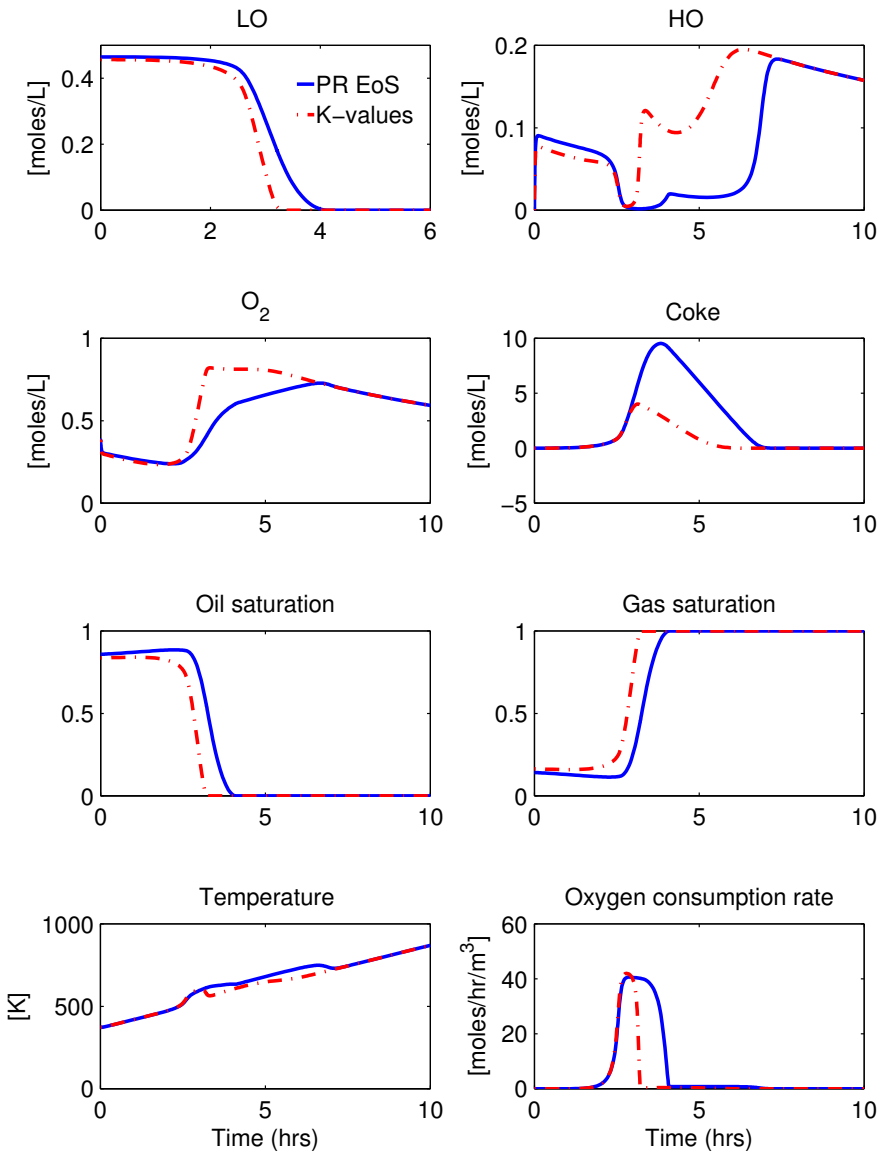

Figure 2. Simulation results for a ramped temperature experiment using the minimal reaction model. Comparison is made between using K-value correlations and the PR EoS for the phase equilibrium description.

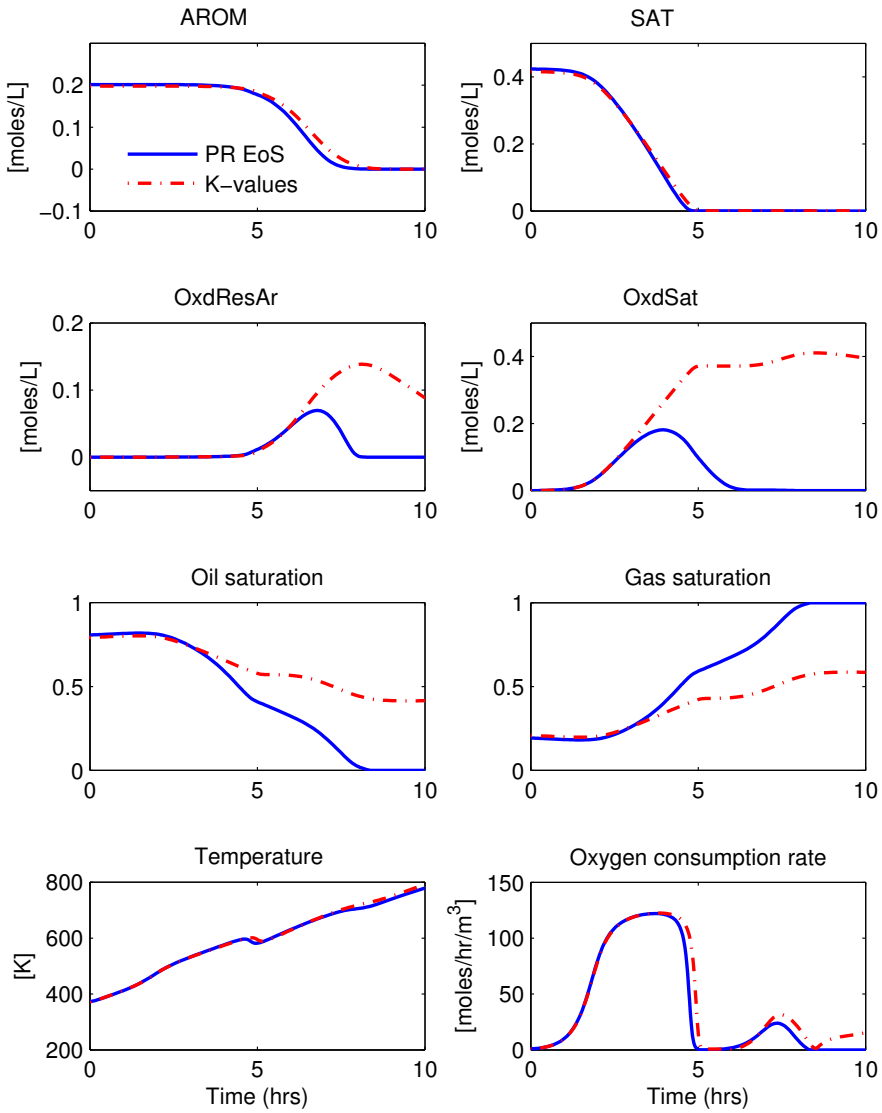

Figure 3. Simulation results for a ramped temperature experiment using the SARA model. Comparison is made between using K-value correlations and the PR EoS for the phase equilibrium description.

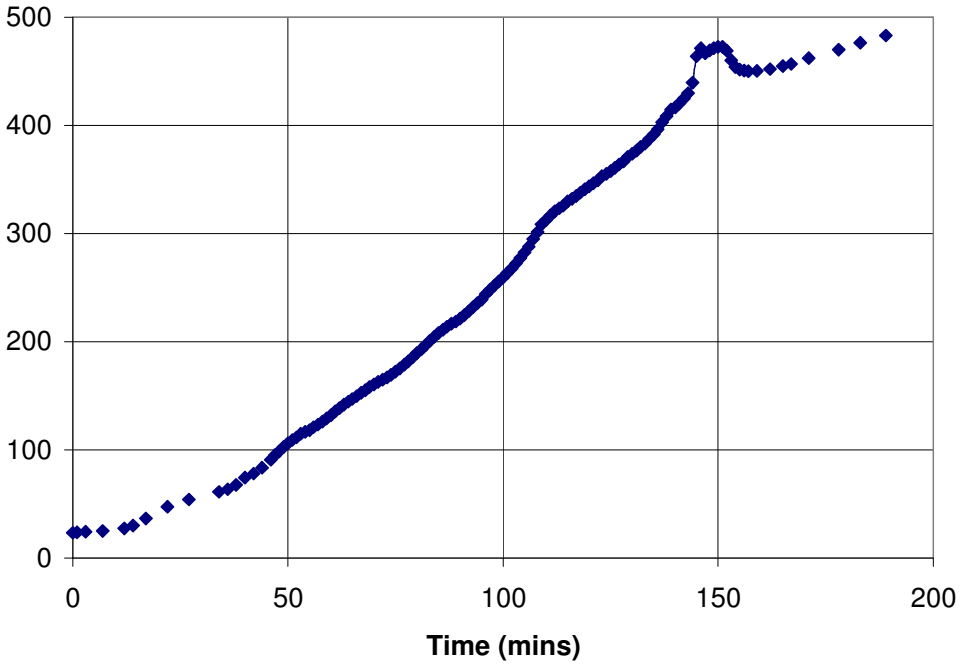

Figure 4. Temperature versus time for ramped temperature oxidation of crushed reservoir matrix with residual hydrocarbon. System pressure is 290 psi and air injection rate is 1.5 l/m.

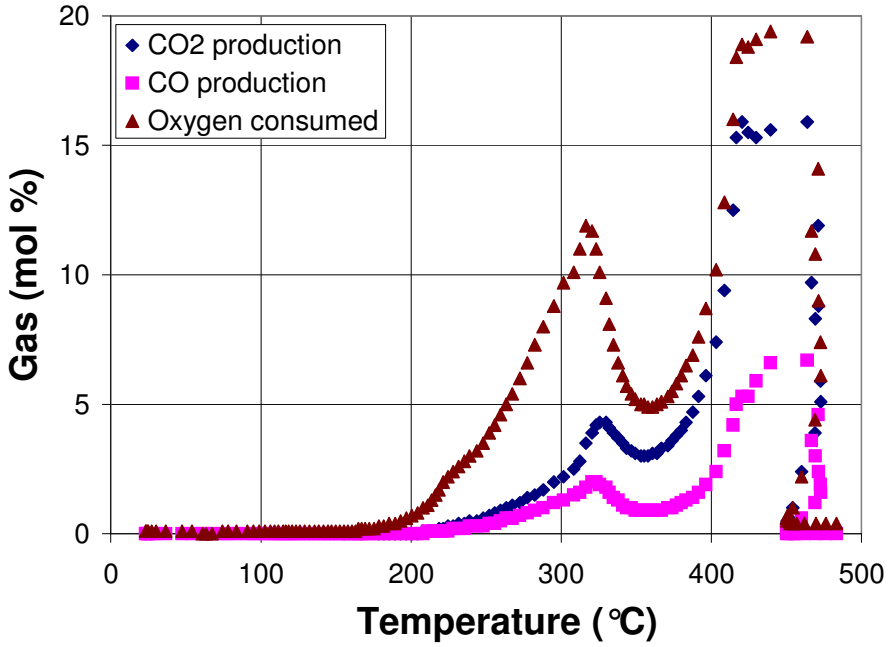

Figure 5. Effluent gas profiles from ramped temperature oxidation of the crushed core with residual hydrocarbon. System pressure is 290 psi and air injection rate is 1.5 l/m.